[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, AND THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Evaluation of Resonance Effects on Reactivity by Application of the Linear Inductive Energy Relationship. V. Concerning a σ_R Scale of Resonance Effects[1,2]

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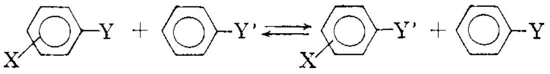
The data for eighty-eight aromatic reaction series (classified according to six reactivity categories) involving uncharged *m*- and *p*-substituents have been analyzed according to the results of quantitative estimation of resonance effects (*R*-values). The results disclose that for neither *m*- nor *p*-substituents does there exist a precise quantitative scale of resonance effects (σ–ρ type relationship) with as wide a scope as for the linear inductive energy relationship, $I = \sigma_I\rho_I$. However, the data for a selected group of *m*-substituents do define precise resonance parameters ($\sigma_R{}^m$) which apply with remarkable precision ($S = 0.03$) and generality to about 90% of the data. A σ_R scale of the same precision and applicability does not apply for *p*-substituents. It is concluded that the *R*-values which arise as a consequence of inductive transmittal through space or the Ar–Y σ-bond (Y = side chain reaction center) of mesomerically distributed charge are rather widely correlated by precise σ–ρ type relationships. On the other hand, the *R*-values which are determined (at least in part) by direct resonance interaction between the substituent and the side chain reaction center follow such relationships for only narrow ranges of reactivity type and reaction conditions. A procedure is recommended for modified use of the Hammett equation in thorough and precise investigations of the reactivity effects of *m*- and *p*-substituents which allows for the identification and study of specific resonance effects.

In a previous paper, a method was proposed for the approximately quantitative evaluation of inductive and resonance contributions to the effects of uncharged *m*- and *p*- substituents on the reactivities of benzene derivatives.[4] This method is based upon the demonstration that the scale (quantitative ordering) of the substituent inductive contributions to aromatic series reactivities is to good approximation equal to that for reactivities in the aliphatic series. The demonstration was made empirically in terms of the relatively precise linear inductive energy relationship (1) $I = \sigma_I\rho_I$, which underlies aromatic reactivities of all types. Included are reactivities which demand for correlation by the Hammett equation,[5] all of the proposed multiple σ-values[5,6,7] (σ, σ^+ and σ^-), as well as some reactivities which do not satisfactorily fall into any of these schemes.

In the present paper and in following members of this series the resonance contributions to aromatic series reactivities are reported, their similarities and contrasts noted, and the results are interpreted in accord with, and are shown to provide evidence for, principles from resonance theory. To the extent that this is successful, evidence is provided for the inspiring basic postulate of Hammett, namely, that the standard free energy change for a series of processes of the type (Y represents a side-chain reaction center in a general reactant of a reaction series and Y′ represents such a group in either the transition state of a rate process or the product state of an equilibrium) is equal to or is linearly related to the electronic work of such a reaction.[8]



The separation of inductive and resonance effects by our method is based upon two assumptions.[4] The primary assumption is that the substituent effect on the free energy change behaves approximately as a sum of an inductive effect, *I*, and a resonance effect, *R* (the sense in which this separation is proposed is discussed further in a later section), *i.e.*

$$\log (k^m/k_0) = I + R^m \qquad (2)$$

$$\log (k^p/k_0) = I + R^p \qquad (3)$$

The subordinate assumption[9] made to accomplish the separation is the apparently less accurate approximation that in a given reaction series the ratio of the *R*-value for the *meta* relative to that of the corresponding *p*- substituent is a constant, α, *i.e.*

$$\alpha = R^m/R^p \qquad (4)$$

The factor, α, may be considered a resonance effect fall-off factor between the *m*- and *p*-positions (*cf.* conclusion section). Taft and Lewis have suggested that very generally $\alpha \cong 0.33$ but that in reactivities in which there is a strong change in conjugation during the reaction process between a *p*-substituent and the first atom of the side-chain, a reduced value of α must be used ($\sim$0.10) because of the enhanced resonance effect (R^p) for the *p*-substituent.[4]

Roberts and Jaffé[10] have made a statistical examination of the fit of available data (excluding distinct nucleophilic and electrophilic reactivities) to the equation (obtained from equations 1–4)

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[1] (1) This work was supported in part by the Office of Naval Research, Project NR055-328. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] (2) Paper IV, R. W. Taft, Jr., and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959).

[3] (3) (a) Alfred P. Sloan Fellow, 1955–1957; (b) John Simon Guggenheim Fellow, Harvard University, Fall term, 1958.

[4] (4) R. W. Taft, Jr., and I. C. Lewis, THIS JOURNAL, **80**, 2436 (1958).

[5] (5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter 7.

[6] (6) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[7] (7) H. C. Brown and Y. Okamoto, THIS JOURNAL, **79**, 1913 (1957).

[8] (8) Reference 5, p. 123.

[9] (9) A third assumption is also made, namely, that $I^m \cong I^p$ (for evidence on this point *cf.* J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, **73**, 2182 (1951); R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957); and B. M. Wepster, *et al.*, *Rec. trav. chim.*, **77**, 509 (1958), and earlier references cited there. In unpublished work we have found that the introduction of a constant, $\gamma = I^m/I^p = \rho_I{}^m/\rho_I{}^p$, having values differing from unity does not significantly improve the agreement between aliphatic and aromatic σ_I-values, or between aromatic σ_I-values derived from various reactivities. In fact, if γ differs from unity beyond ±20%, a significant decrease in the precision of the linear inductive energy relationship results.

[10] (10) J. L. Roberts and H. H. Jaffé, THIS JOURNAL, **81**, 1635 (1959).

TABLE I

COMPARISON OF TYPICAL AROMATIC AND ALIPHATIC σ_I-VALUES

Subst.	σ_I Aliphatic series	Source[a] N.m.r. spectra m-XC_6H_4F[b]	A.13	A.8	A.1	[c]	A.19	B.11	F.2	F.1	σ^m (from McDaniel and Brown[17])	σ_p
CH_3	−0.05	−0.09	−0.03	−0.03	−0.03	−0.09	−0.05	−0.03	−0.06	−0.03	−0.07	−0.17
NH_2	+ .10	+ .11	+ .12	....	+ .04	....	+ .12	....	....	....	− .16	− .66
C_6H_5	+ .10	+ .18[d]	....	....	+ .09	....	....	....	+ .09	....	+ .06	+ .01
OH	+ .25	+ .23	+ .27	+ .24	+ .32	....	....	....	....	....	+ .12	− .37
OCH_3	+ .25	+ .26	+ .20	....	+ .28	+ .26	+ .23	....	....	+ .23	+ .12	− .27
$NHCOCH_3$	+ .28	+ .25	....	....	+ .30	....	....	....	....	....	+ .21	± .00
CH_3CO	+ .28	+ .26	....	....	+ .32	....	....	+ .28	....	....	+ .39	+ .31
CF_3	+ .41	+ .43	....	....	+ .38	....	....	....	....	....	+ .43	+ .54
Br	+ .45	+ .44	+ .45	+ .51	+ .45	+ .50	....	+ .42	....	+ .43	+ .39	+ .23
Cl	+ .47	+ .43	+ .48	+ .52	+ .42	+ .50	+ .47	+ .50	+ .48	+ .43	+ .37	+ .23
F	+ .52	+ .58	+ .48	+ .52	+ .45	+ .52	+ .49	....	....	....	+ .34	+ .06
CN	+ .58	+ .58[d]	+ .56	+ .49	+ .52	....	....	....	+ .56	+ .63	+ .56	+ .66
NO_2	+ .63	+ .63[d]	+ .68	+ .68	+ .68	....	+ .62	+ .65	....	....	+ .71	+ .78
α			.58	.46	.29	.63	.33	.33	.50	.50		
ρ_I			+2.24	+1.32	+1.00	+1.80	+1.29	+1.90	− .80	− .70		

[a] Numbers refer to reaction series as listed in Table II. [b] *Cf.* ref. 11 of text; σ_I-values are calculated from the correlation equation $\delta_{\text{meta}} = 0.61\ \sigma_I - 0.05$. [c] pK_a, *cata* and *epi*-4-chloroquinolinium ions, H_2O, 25°, E. Baciocchi, G. Illuminati and G. Marino, THIS JOURNAL, **80**, 2270 (1958). [d] Based upon δ^F_{meta} values given by Gutowsky, *et al.*, *cf.* ref. 11.

$$\log (k^m/k_0) = \alpha \log (k^p/k_0) + (1 - \alpha)\sigma_I\rho_I \qquad (5)$$

wherein α and ρ_I are reaction constants. These investigators find generally highly precise fits with significant improvement in fit using values of α which vary somewhat from reaction series to reaction series. On this basis, the great predominance of reaction series were found to give values of α from 0.2 to 0.6 with the mean lying in the region of 0.4.

The separation of I and R is made using the appropriate value of α (obtained by using the fixed values of $^1/_3$ or $^1/_{10}$ or by the method of Jaffé, equation 5)

from (2) and (4), $\log (k^m/k_0) = I + \alpha R^p$

from (3) $\alpha \log (k^p/k_0) = \alpha I + \alpha R^p$

Therefore(6) $I = \left(\frac{1}{1 - \alpha}\right) [\log (k^m/k_0) - \alpha \log (k^p/k_0)]$

An I-value can thus be obtained by equation 6 for each substituent if rate or equilibrium data are available for both the m- and p-positions. I-values are then fitted by equation 1, $I = \sigma_I\ \rho_I$, and the value of the inductive reaction constant, ρ_I, is obtained. In many (but not all) instances, the value of ρ_I is equivalent to the ρ-value obtained for m-substituents by the Hammett equation (*cf.* last section of this paper for further discussion of this point).

The generality and the precision of fit of equation 1 appear to justify to useful approximation the general applicability of the σ_I scale of inductive effects. For purposes of comparison with the resonance effects to be considered in this paper, it is useful to demonstrate the precision of the linear inductive energy relationship by a comparison of "σ_I" values. In Table I are collected some *typical* "aromatic" σ_I-values for comparison with the aliphatic σ_I-values[4] (σ_I"aliphatic" $= 0.45\ \sigma^*_{XCH_2}$). The former are obtained for each reaction series by dividing the I-values obtained by equation 6 by the reaction constant, ρ_I. The values of α and ρ_I used to obtain the σ_I-values for each reaction series are also listed. The significance of the α-factor is considered in detail in a subsequent paper. Also shown in Table I are aromatic σ_I-values *obtained directly* ($\sigma_I = (\delta_m{}^F + 0.05)/0.61$) from the shielding effects (chemical shifts) of m-substituents in the n.m.r. spectra of fluorobenzenes in dilute carbon tetrachloride solution.[11] The average deviation of the aromatic and aliphatic σ_I-values of Table I is ±0.03 unit and the deviations are roughly random. Individual deviations rarely exceed ± 0.08 unit.

It cannot be claimed, of course, that the quantitative ordering of inductive effects is precisely independent of reaction type or conditions. The remarkable scope of this approximation, however, is well illustrated by the σ_I-values of Table I. It is worthy of note that the σ_I-values of Table I cover the complete range in solvent variation from water to hydroxylic organic solvents to the non-hydroxylic solvents, dioxane, CCl_4 and benzene.[12] The scope of the linear free energy relationship is further illustrated by the linear relationship between "aliphatic" σ_I-values and the inductive constants, I, which Branch and Calvin[15] derived from the acidities of X–OH compounds in water, 25° ($\sigma_I = 0.059I$; $S = \pm 0.03$).

In considering the significance of the agreement illustrated by Table I it is essential to bear in mind that the σ_I-parameters are unique to aromatic series reactivities in the following sense. It can be stated unequivocally that in no known

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(11) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis and R. E. Glick, THIS JOURNAL, **81**, 5352 (1959).

(12) A measurable variation of the σ_I-value for the OCH_3 group apparently occurs between aqueous solution and non-aqueous media.[13] Both the ionization of methoxyacetic acid[13b] and of methoxyammonium ions[13a] in water give $\sigma_I = +0.29$, whereas $\sigma_I = +0.25$ holds for non-hydroxylic media and for most mixed aqueous organic solvents.[14]

(13) (a) H. K. Hall, Jr., THIS JOURNAL, **79**, 5441 (1957); (b) E. J. King, abstracts of Papers, Am. Chem. Soc. Meeting, New York, Sept., 1957, p. 485.

(14) R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(15) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp. 203-245.

reaction series are the log (k/k_0) values for a variety of *m*- or *p*-substituents correlated by σ_I-values (alone) with anything like the precision of equation 1 (*cf.*, for example, Figs. 3 and 4 of reference 2). Thus *I*-values are derived from quantities which are related to structure in a manner distinctly different from that for the σ_I-parameters. Individual (but not general) exceptions to this statement are known. Taft and Evans have shown that complete steric inhibition of the resonance interactions of p-$N(CH_3)_2$, OCH_3 and NO_2 groups give Hammett σ-values for such groups which are equal to their aliphatic σ_I-values.[16] Table I includes a comparison of corresponding σ_I, σ^{para} and σ^{meta} values as a means of illustrating the unique character of the σ_I-parameters (note, in the above connection, the approximate relationship $\sigma_I \cong \sigma^m$ which is obeyed for several substituents). The σ-values are taken from the recent compilations of McDaniel and Brown[17] (based solely upon the ionization constants for $ArCO_2H$, H_2O, 25°).

The *R*-values for a substituent may be obtained from the rearranged forms of equations 2 and 3, *i.e.*

$$R^m = \log (k^m/k_0) - I = \log (k^m/k_0) - \sigma_I\rho_I \quad (2')$$
$$R^p = \log (k^p/k_0) - I = \log (k^p/k_0) - \sigma_I\rho_I \quad (3')$$

In view of the demonstrated applicability of aliphatic σ_I-values, we believe that the most generally satisfactory method of obtaining *R*-values is through the identification of *I* with $\sigma_I\rho_I$ (as indicated in equations 2′ and 3′). This procedure to considerable extent negates the question of a precisely fixed α-value for each reaction series. Errors introduced in the *I*-values calculated by equation 6 by the inappropriate assumption of a particular α-value (say $^1/_3$ rather than $^1/_2$, for example) are likely to appear as essentially random scatter in a plot of *I vs.* σ_I, and thus, if a sufficient variety of substituents is involved, the least squares regression line of this plot will nonetheless give a reliable value of ρ_I. With this value, the *R*-values may be evaluated by equations 2′ and 3′. At least some part of the deviations between the "aromatic" and aliphatic σ_I-values of Table I (and in general of deviations from the $I = \sigma_I\rho_I$ relationship which exceed the precision measures indicated for Table I), we believe are due to errors introduced by the assumption of a fixed value of α.

In the comparison of *R*-values it is useful to define an "effective" (or specific) resonance parameter as $\bar{\sigma}_R \equiv R/\rho_I$. The utility of this definition results from the fact that deviations from the Hammett equation which result from a specific dependence of resonance effects on reaction type and conditions are immediately detected by the deviation of the given value of $\bar{\sigma}_R$ from the normal value. That is, reactivities which follow the Hammett equation with relatively high precision must yield closely identical $\bar{\sigma}_R$-values and the sum $\sigma_I + \bar{\sigma}_R$ should give the Hammett σ-value. It is worthy of note that by this procedure $\bar{\sigma}_R$ is obtained by assuming (for purposes of comparison but otherwise without complete justification) the relationship $\log (k/k_0) = \rho_I(\sigma_I + \bar{\sigma}_R) = $ "$\rho\bar{\sigma}$". The expression for obtaining the resonance parameter directly is accordingly $\bar{\sigma}_R \equiv (\log (k/k_0)/\rho_I) - \sigma_I$.

The present paper is concerned principally with the evidence bearing on the question of the generality of a commonly followed precise scale of resonance effects in aromatic series reactivities. Subsequent papers deal with the discussion of specific examples of the dependence of resonance effects on reaction type and experimental conditions.

Results

It is first necessary to consider the nature of the separation proposed by Taft and Lewis. Resonance theory clearly anticipates that mesomeric or resonance interactions will generally be accompanied by coöperative and intrinsically associated inductive interactions.[18] Thus specific inductive effects on reactivity which are inherently associated with specific resonance effects of substituents are expected. Yet σ_I-values from aromatic series reactivities are to good approximation equal to those from saturated aliphatic systems (*cf.* Table I) in which resonance interactions are presumably not possible. The clue as to the nature of the $I + R$ separation is thus clearly apparent.

The *I*-values represent that part of the total inductive effect contribution to log (k/k_0) values which is due to inductive interaction through σ- and π-bonds (ionic resonance of bonds) and through space (field effects) for the *hypothetical m*- or *p*-substituted benzene derivative which involves no conjugation (resonance interaction) between the substituent and the benzene ring. Although the *I*-values thus appear to relate to hypothetical molecules, these values are nonetheless obtainable from experimental values of log (k/k_0) by virtue of the approximate relationship $R^p/R^m = \alpha$ as indicated in equation 6. The *I*-values according to this line of reasoning do not include any of the inductive effects which may arise as a consequence of mesomeric interaction—such terms are included in the *R*-values. In other words, *R*-values are measures of the total effect on reactivity resulting from the existence of resonance interaction. If additional interactions other than resonance interactions contribute to the observed reactivities, these too will be included in the *R*-values. The observation of Taft and Evans that complete steric inhibition of resonance interaction of a *p*-substituent results in observed log (k^p/k_0) values which equal $\sigma_I\rho_I$ is consistent with and provides important evidence for this conclusion.[16]

The sense in which Taft and Lewis propose separation of log (k/k_0) values to *I*- and *R*-values bears something of an analogy to the scheme of Pauling for separation of the observed energy of a bond to the sum of that for the normal covalent bond (the energy of the hypothetical bond with no ionic character) and an extra ionic bond resonance energy.[19]

Data for eighty-eight reaction series (listed in Table II) which involve relatively large and as diverse substituent effects as are available and, for

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[16] R. W. Taft, Jr., and H. D. Evans, *J. Chem. Phys.*, **27**, 1427 (1957).

[17] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[18] *Cf.* R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

[19] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p. 47.

TABLE II

SUMMARY OF REACTIONS[a]

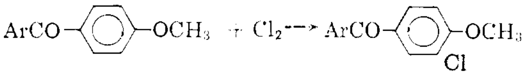
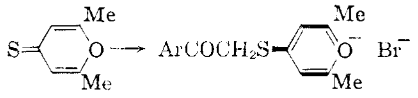
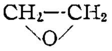
			α	ρI	Ref.[b]
		A. Benzoic reactivities			
A.1.	E.	Ionization $ArCO_2H$, H_2O, 25°	0.29	(+1.00)	1
A.2.	E.	Ionization $ArCO_2H$, 50% aq. ethanol, 25°	.42	+1.50	2, 3, 4
A.3.	E.	Ionization 2-CH_3ArCO_2H, 50% aq. ethanol, 25°	.33	+1.64	5
A.4.	E.	Ionization 2,6-diCH_3ArCO_2H, 50% aq. ethanol, 25°	. .	+1.50[c]	6
A.5.	E.	Ionization $ArCO_2H$, 26.5% dioxane, H_2O, 25°	.45	+1.23	7
A.6.	E.	Ionization $ArCO_2H$, 43.5% dioxane, H_2O, 25°	.48	+1.33	7
A.7.	E.	Ionization $ArCO_2H$, 73.5% dioxane, H_2O, 25°	.46	+1.42	7
A.8.	E.	Ionization $ArCO_2H$, ethylene glycol, 25°	.46	+1.32	7
A.9.	E.	Ionization $ArCO_2H$, methanol, 25°	.52	+1.55	7
A.10.	E.	Ionization $ArCO_2H$, ethanol, 25°	.61	+1.67	7
A.11.	E.	Ionization $ArCO_2H$, 1-propanol, 25°	.62	+1.65	7
A.12.	E.	Ionization $ArCO_2H$, 1-butanol, 25°	.62	+1.56	7
A.13.	E.	Ion-pair formation, $ArCO_2H$ with 1,3-diphenylguanidine, benzene, 25°	.58	+2.24	8
A.14.	R.	$ArCO_2H$ with diphenyldiazomethane, ethanol, 30°	.55	+1.00	2, 9
A.15.	R.	Saponification $ArCO_2Et$, 60% aq. acetone, 25°	.33	+2.33	2, 10
A.16.	R.	Saponification $ArCO_2Et$, 88% aq. ethanol, 30°	.41	+2.50	2, 10
A.17.	R.	Methoxide catalyzed *trans* esterification, $ArCO_2C_{10}H_{19}$, methanol, 40°	.43	+2.70	2
A.18.	E	Ionization, $ArCH{=}CHCO_2H$, H_2O, 25°	.33	+0.47	2
A.19.	R.	Saponification $ArCH{=}CHCO_2Et$, 88% aq. ethanol, 30°	.33	+1.29	2
A.20.	E.	Ionization, $ArC{\equiv}CCO_2H$, 35% aq. dioxane, 25°	.38	+0.70	11
A.21.	E.	Ionization, $ArC{\equiv}CCO_2H$, 50% aq. ethanol, 25°	.32	+0.65	12
A.22.	R.	Acid-catalyzed hydrolysis, $(ArCO)_2O$, 75% aq. dioxane, 58°	.42	+3.20	2
A.23.	R.	$ArCO_2H + HN_3$, trichloroethylene, 40°	. .	−2.20[d]	2
A.24.	R.	Saponification, 5 and 6-substituted phthalides, 15% aq. ethanol, 25°	.32	+1.74	50
		B. Miscellaneous reactivities			
B.1.	E.	Ionization, $ArCH_2CO_2H$, H_2O, 25°	0.50	+0.46	2
B.2.	R.	Saponification $ArCH_2CO_2Et$, 88% aq. ethanol, 30°	. .	+1.00[e]	2
B.3.	E.	Ionization, $ArCH_2CH_2CO_2H$, H_2O, 25°	.60	+0.24	2
B.4.	R.	Saponification. $ArCH_2CH_2CO_2Et$, 88%, aq. ethanol, 30°	. .	+0.75[f]	2
B.5.	E.	Ionization, $ArPO(OH)_2$, H_2O, 25°	.40	+0.73	2
B.6.	E.	Ionization, $ArPO_2(OH)^-$, H_2O, 25°	.40	+1.19	2
B.7.	E.	Ionization, $ArB(OH)_2$, 25% aq. ethanol, 25°	.44	+2.15	2
B.8.	R.	Acid-catalyzed hydrolysis, $ArN{=}C{=}NAr$, 75% aq. tetrahydrofuran, 20°	.33	−1.41	13
B.9.	R.	Solvolysis, $ArSCH_2Cl$, 50% aq. dioxane, 35°	.25	−2.58	14
B.10.	E	$Ar_2SeBr_2 \rightleftarrows Ar_2Se + Br_2$, CCl_4, 25°	.33	+1.96	2
B.11.	R.	Chlorination.  99% aq. acetic acid, 20°	.50	−0.65	2
B.12.	R.	$ArCOCH_2Br$ +  benzene, 25°	.50	+1.03	2
B.13.	R.	2-$NO_2ArNHCOCH_3 + MeO^- \rightarrow CH_3CO_2Me$ + 2NO_2-$ArNH^-$ methanol, 65°	− .45	+1.81	2
B.14.	R.	Saponification benzyl acetates, 60% aq. acetone, 25°	.60	+0.73[d]	51
B.15.	R.	$ArCHO + OH^- \rightarrow ArCOO^- + ArCH_2OH$, 50% aq. methanol, 100°	.41	+3.96[d]	52
		C. Nucleophilic reactivities			
C.1.	E	Ionization, ArOH, H_2O, 25°	0.41, 0.07	+2.36	2, 15, 16
C.2.	E.	Ionization, ArOH, 49% aq. ethanol, 22°	.33, .10	+2.70	2
C.3.	E.	Ionization, ArOH, 95% aq. ethanol, 22°	.40, .10	+2.90	2
C.4.	E.	Ionization, ArSH, 48% aq. ethanol, 25°	.50, .10	+2.70	2, 15,[b] 17
C.5.	E.	Ionization, ArSH, 95% aq. ethanol, 22°	.50, .10	+2.91	2
C.6.	R.	Alkaline methylation, $ArOH + CH_3SO_4^- \rightarrow ArOCH_3$, H_2O, 100°	.33	−0.66	2
C.7.	R.	Alkaline epoxide cleavage, ArOH +  $CH_2{-}CH_2$ (O bridge) $\rightarrow ArOCH_2CH_2OH$, 98% aq. ethanol, 70°	.30	−1.00	2

TABLE II (*continued*)

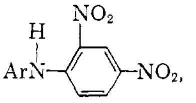
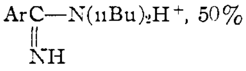
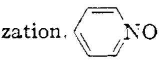
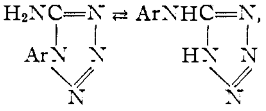
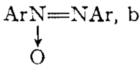
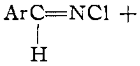
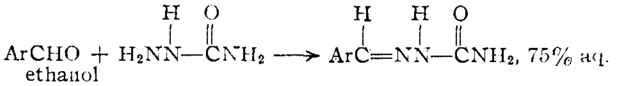
			α		ρ_I	Ref.[b]
C.8.	R.	Alkaline hydrolysis, $ArOSi(Et)_3 \rightarrow ArO^- + Et_3SiOR$, 51% aq. ethanol, 25°	.50		+1.85	18
C.9.	E.	Ionization, $ArNH_3^+$, H_2O, 25°	.28,	.15	+2.90	2, 19, 20, 42, 45
C.10.	E.	Ionization, $ArNH_3^+$, 50% aq. EtOH, 25°	.35		+2.93	21
C.11.	E.	Ionization, $ArNH_3^+$, methanol, 25°	.40,	.10	+4.00	2
C.12.	E.	Ionization, $ArNH_3^+$, ethanol, 25°	.50,	.10	+4.75	2
C.13.	E.	Ionization, $ArNH(CH_3)_2^+$, av. of H_2O, 20°, 25°, and 50% aq. ethanol, 25°	.35,	.10	+3.34	2, 3b, 22
C.14.	E.	Formolysis, $ArNH_2 + HCO_2H \rightleftarrows ArNHCHO$, 66% aq. pyridine, 100°	.33,	.10	−1.47	2
C.15.	R.	$ArNH_2 + C_6H_5NO \rightarrow ArN{=}NC_6H_5$, 94% aq. ethanol, 72.5°	.33,	.10	−2.29	23
C.16.	R.	$ArNH_2 + C_6H_5COCl \rightarrow ArNHCOC_6H_5$, benzene, 25°	.33,	.10	−3.20	2
C.17.	R.	$ArNH_2$ + 2,4-di$NO_2C_6H_3Cl \rightarrow$  ethanol, 100°	.40		−2.87	**2**
C.18.	E.	Ionization  $\underset{\underset{NH}{\|}}{ArC}\text{—}N(nBu)_2H^+$, 50% aq. methanol, 25°	.50		+1.60	2
		D. Electrophilic reactivities				
D.1.	E.	Ionization, $Ar_3COH + H^+ \rightleftarrows Ar_3C^+$, aq. H_2SO_4, 25°	..		−12.05[g]	24
D.2.	E.	Ionization, azobenzene, 20% ethanol, H_2SO_4, 25°	0.33		+2.41	25
D.3.	R.	Solvolysis, $ArC(CH_3)_2Cl$, 90% aq. acetone, 25°	.40,	.10	−4.34	26
D.4.	R.	Solvolysis, $ArCH_2OTs$, 76% aq. acetone, 25°	.10		−2.31	27
D.5.	R.	Solvolysis, $ArCH_2Cl$, 50% aq. acetone, 60°	.45,	.10	−1.43	2
D.6.	R.	Solvolysis, $Ar(C_6H_5)CHCl$, ethanol, 25°	.15		−4.00	2, 28
D.7.	R.	Solvolysis, $Ar(C_6H_5)_2CCl$, 60% ethyl ether–40% ethanol, 60°	..		−2.54[g]	2
D.8.	R.	Beckmann rearrangement, $Ar(CH_3)C{=}NOH$, 1,4-dichlorobutane, 70°	.33		−3.98	29
D.9.	R.	Brominolysis, $ArB(OH)_2$, 20% aq. acetic acid, 25°	.30,	.15	−3.62	30
D.10.	R.	Protonolysis, $ArSi(CH_3)_3$, aq. acetic acid, H_2SO_4, 25°	.10		−4.24	31
D.11.	R.	Nitration, ArH, HNO_3 in acetic anhydride, 25°	.33,	.10	−6.70	32, 33, 34
D 12.	R.	Bromination, substituted mesitylenes and durenes, CH_3NO_2, 30°	.20		−8.69	35
D.13.	R.	$ArB(OH)_2 + H_2O_2 \rightarrow ArOB(OH)_2$, 25% aq. ethanol, 25°	.30		−1.16	36
D.14.	R.	Diazocoupling with 2.6-naphthylamine sulfonic acid, ArN_2^+, H_2O, 20°	.30		+4.15	37
D.15.	R.	Solvolysis, ArCOCl, ethanol, 0°	.33		+1.90	2
D.16.	E.	$ArCHO + HCN \rightleftarrows ArC(OH)CN$, 95% aq. ethanol, 20°	.50,	.18	+0.92	2, 38
D.17.	E.	$ArCOCH_3 + H^+ \rightleftarrows ArCOHCH_3^+$, aq. H_2SO_4, 25°	..		−2.1[d]	46
D.18.	E.	$ArN_2^+ + OH^- \rightleftarrows ArN{=}N\text{—}O^-$, H_2O, 25°	.40		+7.2[d]	47
		E. Amphoteric reactivities				
E.1.	E.	Ionization,  , H_2O, 25°	0.33,	.10	+2.16	39, 40
E.2.	E.	 , ethylene glycol, 197°	.30,	.10	+1.01	41
E.3.	R.	$E_{1/2}$. Polarographic oxidation, $ArNH_2$, H_2O, pH 7.0, 25°	.34,	.10	+0.25[h]	42
E.4.	R.	Decomposition, ArN_2^+, H_2O, 29°	−.65		−4.21	43
E.5.	R.	$ArN{=}NAr + C_6H_5CO_3H \rightarrow$  $\underset{\underset{O}{\downarrow}}{ArN}{=}NAr$, benzene, 25°	.30,	.10	−1.29	2
E.6.	R.	$ArOSO_3H + H_3O^+ \rightarrow ArOH + H_2SO_4$, H_2O, 49°	.12		+0.54	2
E.7.	R.	 $\underset{\underset{H}{\vert}}{ArC}{=}NCl + OH^- \longrightarrow ArC{\equiv}N$, 93%, aq. ethanol, 0°	.50,	.30	+2.13	2
E.8.	R.	 $ArCHO + H_2N\overset{\overset{H}{\vert}}{N}\text{—}\overset{\overset{O}{\|}}{C}NH_2 \longrightarrow Ar\overset{\overset{H}{\vert}}{C}{=}N\overset{\overset{H}{\vert}}{N}\text{—}\overset{\overset{O}{\|}}{C}NH_2$, 75% aq. ethanol	....		−0.30[d]	48
		F. Radical reactivities				
F.1.	R.	Decomposition, $(ArCO)_2O_2$, dioxane, 80°	0.50		−0.70	2

TABLE II (*continued*)

			α	ρ_I	Ref.[b]
F.2.	R.	Chlorination, $ArCH_3$, liquid hydrocarbons, 70°[c]	.50	− .80	44
F.3.	R.	Decomposition, $(ArCO)_2O_2$, acetophenone, 80°	.48	− .54	2
F.4.	R.	Initiation of polymerization of styrene by $(ArCO)_2O_2$, styrene, 60°	.46	− .88	2
F.5.	R.	Free radical bromination, $ArCH_3$ with N-bromosuccinimide, CCl_4, 80°	.21	−1.51	49

[a] The symbol R designates data for a reaction rate process and E designates an equilibrium process. The basis for the classification of reactivities in Table II is as follows: A. Benzoic reactivities: Ionization of $ArCO_2H$ and saponification rates of the corresponding esters, including systems in which the benzene ring is connected to the CO_2R group by an unsaturated link, *e.g.*, saponification rates of $ArCH{=}CHCO_2Et$, or ionization of $ArC{\equiv}CCO_2H$. B. Miscellaneous reactivities: Reactivities for which in general the $\bar{\sigma}_R{}^p$ values for both $-R$ and $+R$ substituents are not enhanced in magnitude compared to the values for corresponding substituents in A. C. Nucleophilic reactivities: Reactivities for which in general $+R$ substituents have $\bar{\sigma}_R{}^p$-values which are enhanced in magnitude compared to the values for corresponding substituents in A. D. Electrophilic reactivities: Reactivities for which in general $-R$ substituents have $\bar{\sigma}_R{}^p$ values which are enhanced in magnitude compared to corresponding values in A. E. Amphoteric reactivities: Reactivities for which in general both $-R$ and $+R$ substituents have $\bar{\sigma}_R{}^p$-values which are enhanced in magnitude (or are of opposite sign) compared to corresponding values in A. F. Radical reactivities: Self-descriptive. [b] Table references are (1) to (52) below rather than those cited in the text. [c] ρ_I-value assessed to be the same as for reaction A.2. [d] ρ_I-value obtained as ρ^m based upon the procedure recommended in this manuscript. [e] ρ_I-value taken as 1/2.5 ρ_I for reaction A.16; *cf.* ref. 4. All log (k/k_0) have been adjusted by −0.09. This intercept correction is required to give $\bar{\sigma}_R$-values for NO_2, Cl, CH_3 and CH_3O which are in good agreement with the corresponding values from reactions B.1, B.3 and B.4. [f] ρ_I taken as ρ based on the *p*-Cl substituent. [g] ρ_I-value taken as ρ based upon the NO_2 substituent. [h] In volts.

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which sufficient information exists to make reliable separations, have been analyzed for $\bar{\sigma}_R$-values. *The results show clearly the anticipated result that in general no common scale of resonance effects exists which is as nearly independent of reaction type and conditions as is the σ_I scale of inductive effects.*[4,5,6,7,20,21] In fact numerous examples are obtained which show a high degree of specificity of the resonance effects to reaction type and conditions. In other words, precise linear correlations between *R*-values are much more dependent upon reaction type and conditions than are the correlations of *I*-values by equation 1.

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TABLE III

RANGES OF $\bar{\sigma}_R^{para}$ VALUES

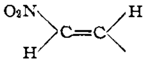
Reactivity class subst.	A. Benzoic	B. Miscellaneous	C. Nucleophilic	D. Electrophilic	E. Amphoteric	F. Radical
NMe_2	−0.82	−0.97	−0.22 to −0.36	−1.38	+4.6 to −1.53	
NH_2	− .46 to − .90	− .24 to −0.76	− .54	−1.30 to −1.70	−0.87 to −2.12	
$NHCOCH_3$	− .28 to − .39	− .30			−1.12	
OH	− .39 to − .63	− .37 to − .38	− .62	−0.94 to −1.11	−0.98	
OCH_3	− .40 to − .64	− .30 to − .60	− .34 to − .57	− .64 to −2.14	+1.23 to −1.29	−0.73 to −1.30
SCH_3	− .25 to − .31		− .04 to − .18	− .59 to −0.92	−1.27	
F	− .35 to − .46	− .37 to − .45	− .44 to − .51	− .40 to − .70	−0.40 to −0.59	−0.38
Cl	− .18 to − .29	− .17 to − .26	− .17 to − .28	− .26 to − .40	+ .18 to − .50	− .30 to −0.37
Br	− .15 to − .24	− .14 to − .25	− .16 to − .23	− .21 to − .35	− .24 to − .49	− .30 to − .31
I	− .11 to − .16	− .11 to − .14	− .06 to − .15	− .16 to − .34	− .48	− .25
CH_3	− .05 to − .15	− .08 to − .15	− .05 to − .15	− .17 to − .59	+ .33 to − .39	− .17 to − .21
C_6H_5	− .08 to − .11	− .01	+ .02 to + .09	− .20 to − .47	+ .21	− .18 to − .35
Me_3Si	+ .05 to + .14		+ .20 to + .23	+ .14		
CF_3	+ .02 to + .13		+ .28 to + .31	+ .20		
CN	− .01 to + .16	+ .04 to + .20	+ .25 to + .41	+ .05 to + .14	+ .09	+ .03 to − .25
CO_2R	+ .13	+ .12 to + .15	+ .19 to + .44	+ .09 to + .31	+ .04 to + .30	
SO_2CH_3	+ .13 to + .19		+ .16 to + .51			
CH_3CO	+ .22		+ .35 to + .58		+ .30	
NO_2	+ .06 to + .23	+ .04 to + .23	+ .27 to + .67	+ .09 to + .26	+ .55 to − .30	− .64 to +1.13
	− .11		+ .43			

TABLE IV

RANGES OF $\bar{\sigma}_R^{meta}$ VALUES

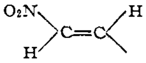
Reactivity type subst.	A. Benzoic	B. Miscellaneous	C. Nucleophilic	D. Electrophilic	E. Amphoteric	F. Radical
NMe_2	−0.25 to −0.26		−0.06 to −0.16			
NH_2	− .20 to − .26	−0.07 to −0.18	− .06		−0.29 to −0.75	
$NHCOCH_3$	− .04 to − .13				− .45	
OH	− .10 to − .35	− .15 to − .18	− .08 to − .14			
OCH_3	− .17 to − .22	− .16 to − .28	− .14 to − .21	−0.16 to −0.28	− .16 to − .44	−0.17 to −0.61
SCH_3	− .10 to − .13		− .02 to − .06	− .07 to − .08	− .22	
F	− .15 to − .25	− .15 to − .20	− .11 to − .21	− .09 to − .17	− .11 to − .16	− .19
Cl	− .08 to − .17	+ .08 to − .17	− .05 to − .16	+ .01 to − .14	.00 to − .33	− .14 to − .19
Br	− .04 to − .18	+ .08 to − .18	.00 to − .09	+ .03 to − .11	− .04 to − .20	− .04 to − .15
I	− .01 to − .09	+ .02 to − .07	+ .03 to − .05	+ .02 to − .07	− .20	− .06
CH_3	+ .04 to − .09	+ .01 to − .09	+ .03 to − .05	+ .03 to − .09	+ .04 to − .17	+ .00 to − .10
C_6H_5	− .04		+ .01 to + .05	+ .01 to + .02	− .19	− .16
Me_3Si	− .06 to + .13		+ .05 to + .11	+ .13		
CF_3	+ .01 to + .05		− .03 to + .13	+ .03 to + .16	+ .00	
CN	− .02 to + .09		+ .06 to + .09	+ .03 to + .11		− .04 to + .05
CO_2R	+ .05 to + .06	+ .07 to + .08	− .02 to + .05	+ .01 to + .10	.00 to + .03	
SO_2CH_3	+ .01 to + .08		+ .08 to + .11			
CH_3CO	+ .08 to + .10	+ .06	+ .03 to + .09	+ .05	+ .02 to + .10	
NO_2	+ .04 to + .12	− .02 to + .11	+ .03 to + .14	+ .03 to + .14	− .03 to + .09	−0.53 to + .51
	− .05		+ .01			

Table III lists the ranges of values of $\bar{\sigma}_R$ for *p*-substituents according to the six qualitative reactivity categories into which the eighty-eight reaction series have been assigned in Table II (the assignment has been made both on the basis of reaction type and $\bar{\sigma}_R$-values (*cf.* footnote *a* of Table II). Table IV lists corresponding results for *m*-substituents. A range limited to about 0.10 σ unit may be considered excellent for a sharply defined $\bar{\sigma}_R$-value (the "aromatic" σ_I-values calculated from the data for each reaction series fall into this category; *cf.* Table I).

The results of Table III show that no *p*-substituent gives $\bar{\sigma}_R$-values which are limited to such a range in all known reactivities. Several examples are provided for which the sign of the $\bar{\sigma}_R^p$-value depends upon reaction type. The resonance parameters for *m*-substituents conform much more closely to "immutable" behavior as shown in Table IV. However, even for *m*-substituents a number of examples are available for which $\bar{\sigma}_R^m$ values cover at least a threefold variation (*cf.* NMe_2, NH_2, OCH_3) and, in the case of *meta* CN and NO_2 substituents, the $\bar{\sigma}_R$-values for some radical reactivities are of opposite sign to those for ionic reactions.

The results shown in Tables III and IV pose the question as to whether there exists a limited scale of resonance effects of sufficient precision and generality to be useful for prediction and correlation of well defined reactivities. The wide success of the Hammett equation implies that such a scale does exist. Taft has proposed[11,15] a σ_R-scale of resonance effects obtained as $\sigma_R = \sigma - \sigma_I$. The initial values of σ_R which were assigned to a number of substituents were based upon the σ-values listed by Hammett[5] or by Jaffé.[6] More recent values have been obtained from average σ-values based solely upon data for the ionization of benzoic acids in water and for the saponification rates of benzoates in aqueous acetone and aqueous ethanol.[22]

The $\bar{\sigma}_R$-values obtained in the present investigation disclose highly general and precise norms for a

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[22] R. W. Taft, Jr., N. C. Deno and P. S. Skell, *Anal. Rev. Phys. Chem.*, 9, 292 (1958).

TABLE V

$\sigma_R{}^m$ AND σ^m VALUES

Sub-stituent	$\sigma_R{}^m$	S	σ_m	n						n_t	%	Exclusions
				A	B	C	D	E	F			
OCH_3	−0.19	0.03	+0.10[a] + .06[b]	13	3	9	8	5	1	46	85	B-3, D-8, E-3, E-4, F-1, F-3, F-4
F	− .17	.03	+ .35	12	6	6	5	3	1	35	94	A-12, D-4
Cl	− .10	.03	+ .37	19	9	18	14	4	3	74	91	B-13, D-4, D-5, E-2, E-8, F-1, A-23
Br	− .07	.03	+ .38	15	6	9	11	2	2	52	87	A-3, B-12, B-13, D-5, E-4, F-4, A-23
I	− .04	.03	+ .35	14	2	5	7	0	1	35	83	B-8, C-3, C-5, D-5, E-3, B-14
CH_3	− .02	.03	− .07	21	8	16	16	5	3	72	96	E-3, E-4, F-4
H	.00		.00	24	15	18	18	8	5	88	100	
CH_3CO	+ .06	.03	+ .34	2	1	6	1	2	0	12	100	None
NO_2	+ .07	.03	+ .70	23	7	12	9	6	1	65	89	A-3, B-13, D-11, D-16, E-3, F-3, F-4

[a] Value for pure aqueous solutions, *cf.* footnote 12. [b] Value for non-aqueous solutions, *cf.* footnote 12.

TABLE VI

APPARENT $\sigma_R{}^m$ AND σ^m VALUES

Substituent	$\sigma_R{}^m$	S	σ_m	n						n_t	%	Exclusions
				A	B	C	D	E	F			
$SOCH_3$	+0.00	0.02	+0.53	3	0	1	0	0	0	4	100	None
CF_3	+ .01	.02	+ .42	3	0	1	1	1	0	8	80	C-13, D-3
CN	+ .04	.04	+ .62	8	0	2	3	0	2	17	89	A-23, F-2
CO_2R	+ .04	.04	+ .36	3	2	7	5	2	0	20	95	E-4
SO_2CH_3	+ .07	.03	+ .66	3	0	3	0	0	0	6	100	None

select number of *m*-substituents. At least 83% of all of the available $\bar{\sigma}_R{}^m$-values for these substituents define norms which are in each case precise to a standard error of ±0.03 unit. In addition these norms are defined by $\bar{\sigma}_R{}^m$-values from at least five of the six reactivity categories. We believe that this uniform high precision (closely similar to that for the σ_I-scale) and general applicability (enormous reactivity ranges and experimental conditions are encompassed) is significant and that it affords a sufficiently critical criterion for defining a useful σ_R-scale of resonance effects.

The results for the select group of *m*-substituents are summarized in Table V which lists mean values (based upon at least twelve $\bar{\sigma}_R{}^m$-values) as $\sigma_R{}^m$. The corresponding Hammett σ-value derived from the value of $\sigma_R{}^m$ ($\sigma^m = \sigma_R{}^m + \sigma_I$) is also given. In no case are these σ-values different from those originally assigned by Hammett by more than the standard error. *This result indicates that* $\rho^m = \rho_I$ *to a precision satisfactory for the* σ_R*-scale* (*cf.* further discussion in section on recommended procedure). Further listed in Table V are the number of values, n, on which the $\sigma_R{}^m$-value is based in each reactivity category, the total number, n_t, of $\bar{\sigma}_R$-values available for the given substituent, the percentage of the total, on which the mean value is based, and a listing of the specific $\bar{\sigma}_R$-values which do not conform to the mean (deviation from average $\geqq \pm 0.08$[23]).

Many of the relatively few excluded values of Table V probably arise from random experimental errors. However, some trends are apparent which are undoubtedly real. Thus several of the available $\bar{\sigma}_R{}^m$-values for the OCH_3 and NO_2 groups from radical reactivities (F) deviate substantially from the $\sigma_R{}^m$-value. The large deviations of the CH_3O and CH_3 groups in reaction series E-4 and E-5 may be associated with the fact that phenyl cation reactivities are involved.

Within the precision herein established for the σ_R-scale, no $\sigma_R{}^m$-value can be given for the NH_2 or the $N(CH_3)_2$ (also apparently for the SCH_3) groups which has a high degree of generality outside of benzoic reactivities (A). Limited to such reactivities, very precise norms exist for these groups which are widely independent of reaction conditions (for NH_2 av. $\bar{\sigma}_R{}^m = -0.24$, $S = \pm 0.02$, $n = 9$; for $N(CH_3)_2$ av. $\bar{\sigma}_R{}^m = -0.25$, $S = 0.00$, $n = 3$; for SCH_3 av. $\bar{\sigma}_R{}^m = -0.12$, $S = \pm 0.02$, $n = 3$; corresponding σ^m values are: −0.14, −0.15 and +0.13, respectively). The very strong dependence of $\bar{\sigma}_R$-values for *meta* and *para* NH_2 and $N(CH_3)_2$ groups on reactivity type and conditions is discussed in detail in a subsequent paper.[11]

The $\bar{\sigma}_R{}^m$-values for the OH group are strongly solvent dependent[6] even when limited to benzoic reactivities (A) and no σ_R-value can be given (in keeping with the precision criterion) for this substituent.

While there is some likelihood that a σ_R-scale is justified for the *m*-substituents, CF_3, CN, CO_2R, $SOCH_3$ and SO_2CH_3, insufficient data are presently available to define norms of the same precision and generality as that established in Table V. Table VI lists as apparent $\sigma_R{}^m$-values the mean values obtained for these groups.

If the same high standards are imposed as a criterion for a σ_R-scale for *p*-substituents, then there exists no *p*-substituent capable of meeting these requirements, and in this sense, no σ_R-scale of resonance effects is justified for *p*-substituents. Thus σ_R-values previously listed[22] for *p*-substituents have been premature from the standpoint of precise general applicability and must be regarded as mean $\bar{\sigma}_R{}^p$-values for the reaction series on which they are based.

If certain reasonably definite restrictions are

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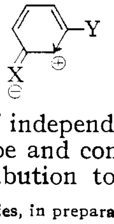
[23] For a quantity having a standard error of 0.03 (based upon at least thirty samples) the odds against a deviation of 0.08 (or greater) are approximately 150 (or greater) to 1. We believe that our results indicate that such odds serve as a realistic (but arbitrary) basis for exclusion of individual $\bar{\sigma}_R$-values from the σ_R-scale.

imposed, $\bar{\sigma}_R$-values for a number of *p*-substituents do define mean values of the desired precision which possess appreciable generality.[11] Practical categorization of $\bar{\sigma}_R{}^p$-values is sometimes achieved by appropriate consideration of reactivity type or of the solvent.[11,24] Improvement in the definitions of reactivity categories necessarily awaits further experimental results and a further understanding of *R*-values or $\bar{\sigma}_R$-parameters.

As illustrated by the ranges of $\bar{\sigma}_R{}^p$-values of Table IV there is little cause for optimism that a single value of σ^+ or σ^- will suffice for the precise description of broad ranges of reactivity in electrophilic and nucleophilic reactivities, respectively. On the other hand, one may be hopeful of eventually achieving sufficiently well defined categories to make precise predictions and correlations.

No reaction series are included in Table II which differ from those listed solely by variation in temperature. The effect of temperature is of much interest and we have accordingly examined the effect of this variable separately. It is unfortunate that few reaction series with the data required to achieve $I + R$ separations have been studied for a temperature interval of at least twenty degrees. As a consequence, little additional can be added to previous discussions of the effect of temperature and the Hammett equation.[5,6,25] The following reaction series give $\bar{\sigma}_R$-values which are in every instance temperature independent (for the temperature range indicated) within ±0.04 unit: A-15 (273–313°K.); A-17 (303–323°K.); B-14 (273–313°K.); C-15 (313–346°K.); C-16 (298–343°K.); A-22 (331–353°K.). In addition, the ρ_I-values in every instance are inversely proportional to the absolute temperatures within their precision. The same results are obtained for reactions D-3 (273–328°K.) and D-5 (303–333°K.) except that variations of $\bar{\sigma}_R$-values by as much as ±0.08 unit are noted in a few instances.

Conclusions.—The generality and relative high precision of the σ_R-scale for the select group of *m*-substituents (Table V and VI) may be attributed to the fact that there is no appreciable direct delocalization of charge from the *m*-position.[11] Consequently, the resonance interaction of the *m*-substituent with the aromatic system is not readily affected by the functional group. Despite the fact that no appreciable direct resonance interaction is involved, the $\sigma_R{}^m$-values in general are finite resonance parameters because of the partial inductive transmission to the reaction center of the charge developed at the *o*- and *p*-positions by the resonance interaction of the *m*-substituent.[4] This second-order mesomeric action is schematically illustrated by the arrow in the following v. b. resonance form (X = *m*-substituent; Y = reaction center)



The high degree of independence of the $\sigma_R{}^m$-values on reactivity type and conditions implies that the fractional contribution to the resonance hybrid of resonance forms such as that given above is to a good approximation widely independent of the nature of the solvent and of the functional group, Y. The limitation of the σ_R-scale to certain selected *m*-substituents, however, indicates that the order of electron release by resonance interaction with the benzene ring can be effected for certain substituents (NH_2 and SCH_3, for example) by strongly polarizing functional groups.[11,26,27]

It is worthy of note in concluding the present discussion that the classification of reactivity effects according to the inductive or resonance categories depends upon the arbitrarily selected cite of reference in the molecule.[28] With respect to the Ar–Y bond, the effect under discussion above is classified as an inductive effect. However, with respect to the Ar–X bond, it must be classified as a resonance effect. It is the latter classification which has been adopted throughout the present paper in referring to the resonance effect (*R*-value). The effect of the resonance interaction of *m*- (and certain *p*-) substituents, for which the above dual classification is applicable, has been termed a resonance polar effect.[28]

A Recommended Procedure.—On the basis of present findings, the following procedure is recommended for thorough and precise investigations of the effects of *m*- and *p*-substituents on the reactivity of benzene derivatives. To establish the value of $\rho_I(= \rho)$ it is essential to determine log (k/k_0) values for the *m*-substituents of Tables V and VI (a minimum of hydrogen and four substituents covering the maximum possible range in σ-values). This procedure may be considered to give a reliable value of $\rho_I = \rho$ if the σ-values calculated for these substituents from best fit of the experimental log (k/k_0) values to the Hammett plot agree with the Hammett σ-values (Table V) within ±0.07 unit and the standard error is not greater than ±0.03. *p*-Substituents which follow the σ–ρ relationship within this precision may now be included (for appropriate systems, σ^0-values which are defined and discussed in the following paper[11] should be used). In no case should the $\rho_I = \rho$ value be based upon *m*- or *p*-substituents for which the calculated σ-values (using the $\rho_I = \rho$ value based upon the appropriate *m*-substituents *only*) deviate from the Hammett σ-values (Tables V and VI or ref. 17) by more than this limit. The present work has repeatedly disclosed that important and significant specific resonance effects of *m*- and especially of *p*-substituents are overlooked if such a procedure is not followed.[11,24]

In the event that the data for the select group of *m*-substituents do not meet the precision requirements given above, one may resort to equation 5 for the determination of the value of $\rho_I = \rho$. In any event, it is desirable to establish by this equation that the linear inductive energy relationship, $I = \sigma_I\rho_I$, is of satisfactory precision. The value of ρ_I obtained by equation 5 also serves as a consistency check on the value obtained by the above procedure.

Data for *p*-substituents (as well as any *m*-substituents) which do not meet the above precision

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(24) Paper VII of this series, in preparation.

(25) J. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(26) Reference 6, p. 231.

(27) P. L. Corio and B. P. Dailey, THIS JOURNAL, **78**, 3043 (1956).

(28) Reference 14, p. 570.

requirements should be analyzed by calculation of R and $\bar{\sigma}_R$-values ($R = \log (k/k_0) - \sigma_I\rho$; $\bar{\sigma}_R = R/\rho$). Correlation of these resonance parameters with corresponding values for potentially similar reaction processes may then be attempted. Several alternate (but not necessarily equivalent) procedures may be used in attempting these correlations. The values of $\bar{\sigma}_R$ for the reaction series of interest may be compared directly with corresponding $\bar{\sigma}_R$-values for reaction series which are expected to be of the same reactivity category. If the values agree for a wide variety of substituents for two or more pairs of reaction series within the precision indicated above, a precise correlation of the unique resonance effects is demonstrated. Alternately, the corresponding values of R in two reaction series may be plotted one *vs.* the other to determine if a precise correlation of the resonance effects exists. Finally, if the reaction series of interest is expected by its nature to show resonance effects closely related to those for a limited reactivity category which has been previously demonstrated to show (within the category) generalized resonance effects which are precisely correlated by a characteristic set of resonance parameters (as, for example, the $\sigma_R{}^0$-values discussed in paper VI),[11] a plot of the R values *vs.* these resonance parameters ($\sigma_R{}^0$, for example) may be made. A satisfactorily precise correlation should be judged by the same precision criterion given above for σ^m-values. Examples of the utility of plots of R-values *vs.* $\sigma_R{}^0$-parameters are discussed in paper VI of this series.[11]

The establishment of precise linear correlations between unique resonance effects in closely related reactivities offers a major tool in the determination of the properties of transition states in reaction mechanism studies. Similar correlations for equilibria provide valuable information on the nature of resonance interactions. It is the very appreciable dependence of the precise order of resonance effects of substituents on the reactivity type and conditions which makes these correlations of especial utility.

The modification we here propose is in no way intended to discredit the many useful purposes for which the original form of the Hammett equation serves quite adequately.[5,6,14] Our purpose is to provide a soundly based procedure which may be used by investigators whose intent is to obtain a more intimate understanding of the effects of structure on reactivity than is permitted by the relationship in its original form.

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[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Evaluation of Resonance Effects on Reactivity by Application of the Linear Inductive Energy Relationship.[1,2] VI. Concerning the Effects of Polarization and Conjugation on the Mesomeric Order

BY ROBERT W. TAFT, JR.,[3] STANTON EHRENSON,[4] IRWIN C. LEWIS AND RICHARD E. GLICK

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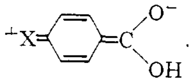
Results from reactivity analysis are reported which show the quantitative mesomeric order of $-R$ substituents in benzene derivatives can be strongly affected by polarization by the functional group. By consideration of resonance effects (R-values) of $-R$ *p*-substituents in reactivities in which conjugation with and/or strong polarization by the reaction center is precluded in either state of the reactivity, a precise quantitative scale of the power of mesomeric charge delocalization by $-R$ substituents is derived. Evidence is presented indicating that so long as the basic requirements for applicability of this $\sigma_R{}^0$ scale are met, the scale holds widely independent of reaction type or conditions. By means of the $\sigma_R{}^0$ scale it is shown that the effects of *p*-substituents, such as NH_2, OCH_3, etc., on the ionization of aqueous benzoic acids include important electromeric contributions. The difference $\bar{\sigma}_R{}^p - \sigma_R{}^0$ (where $\bar{\sigma}_R{}^p$ is the specific resonance parameter for the ionization of benzoic acids in water) is the contribution to the Hammett σ-value resulting from the isovalent conjugation (canonical) form:



. The shielding parameters (chemical shifts) for an extensive series of *m*- and *p*-substituents in the n.m.r. spectra of fluorobenzenes in dilute carbon tetrachloride solution have been determined. The results correspond closely to those obtained originally by Gutowsky in mixed liquid fluorocarbons. For *m*-substituents, the relationship, $\delta_m{}^F = 0.61\ \sigma_I - 0.05$, is followed to high precision (av. dev. = ± 0.035). *para* $-R$ substituents follow the relationship, $\delta_p{}^F = 0.90\ \sigma_I + 3.06\ \sigma_R{}^0 - 0.08$, to the same precision. The latter correlation corroborates the conclusions reached concerning the $\sigma_R{}^0$ scale of resonance effects. *para* $+R$ substituents give $\delta_p{}^F$ values with enhanced resonance contributions which are solvent dependent. Application of the $\sigma_R{}^0$ scale for estimation of special resonance and polarization effects in reactivities and physical properties is illustrated.

In previous papers of this series it has been shown that the effects of uncharged *m*- and *p*-substituents on the reactivities ($\log (k/k_0)$ values) of benzene derivatives may be treated as the sum of inductive and resonance parameters, I and R values, respectively.[2] The I-values follow with great generality and relatively high precision the Hammett-like linear inductive energy relationship,[5] $I = \sigma_I\rho$ (the ρ value used throughout the present papers refers to that obtained by the procedure proposed in ref. 2).

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(1) This work was supported in part by the Office of Naval Research, Project NR055-328. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Paper V, R. W. Taft, Jr., and I. C. Lewis, THIS JOURNAL, **81**, 5343 (1959). Paper V should be consulted for references to the earlier literature.

(3) (a) Alfred P. Sloan Fellow, 1955–1957; (b) John Simon Guggenheim Fellow, Harvard University, Fall term, 1958.

(4) Alfred P. Sloan Postdoctoral Fellow, 1956–1958.

(5) R. W. Taft, Jr., and I. C. Lewis, THIS JOURNAL, **80**, 2436 (1958).